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- (71) Applicant (*for all designated States except US*): **HUH-TAMAKI VAN LEER LTD.** [GB/GB]; Rowner Road, Gosport, Hampshire, PO13 0PR (GB).
- (72) Inventor; and
- (75) Inventor/Applicant (*for US only*): **CARSON, James** [GB/GB]; 42 Bramblewood Manor, Banbridge, Co. Down BT23 4RD, Northern Ireland (GB).
- (74) Agents: **COLMER, Stephen, Gary** et al.; Mathys & Squire, 100 Grays Inn Road, London WC1X 8AL (GB).
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(54) Title: MICROWAVEABLE LONG LIFE CONTAINERS

(57) Abstract: A multi-layer plastics sheet which comprises a gas barrier layer; a tie layer disposed contiguously on either side of layer; one or more external layers of plastics material adhered contiguously to one of the tie layers; and an internal layer of plastics material which includes an oxygen scavenger, the layer being adhered contiguously to the other of the tie layers.

MICROWAVEABLE LONG LIFE CONTAINERS

This invention relates to a plastics sheet. More particularly, this invention relates to a multi-layer plastics sheet suitable for fabricating into containers, especially for perishable goods such as food and drink.

Hitherto, the long life (i.e. shelf life of one year or more) container of choice for perishable goods has been the traditional tin can. Plastics containers for perishable goods are well known and, unlike tin cans, their contents can successfully be heated by irradiation with microwaves. However, such containers do not provide a long shelf life for perishable contents. This is particularly the case where the contents are both cooked and sterilised; for example, by an aseptic filling (hydrogen peroxide sterilisation) or by a water immersion or a steam retort process.

This invention seeks to provide plastics sheet suitable for fabricating into containers which are microwaveable and which also provides a long life for perishable contents.

According, therefore, to one aspect of this invention, there is provided a multi-layer plastics sheet which comprises

- i) a gas barrier layer;
- ii) a tie layer disposed contiguously on either side of layer i);
- iii) one or more external layers of plastics material adhered contiguously to one of the tie layers ii); and
- iv) an internal layer of plastics material which includes an oxygen scavenger, the layer being adhered contiguously to the other of the tie layers ii).

Suitably, the sheet may further comprise a layer of plastics material v) contiguously adhered to

layer iv) and not including an oxygen scavenger.

In a preferred embodiment of the invention, layer i) may comprise polyvinyl alcohol or an ethylene-vinyl alcohol copolymer, suitably wherein the degree of hydrolysis of the polyvinyl alcohol may be from 70 to 90 %. It is preferred that the vinyl alcohol content of the ethylene-vinyl alcohol copolymer may be from 50 to 75 %, preferably 55 to 70, such as 68 % weight. The ethylene content of the copolymer may be from 25 to 45 %, preferably 30 to 40 % by weight.

Suitably, each tie layer ii) may comprise a graft copolymer of an unsaturated carboxylic acid or unsaturated carboxylic acid anhydride with the polymer of the plastics material contiguous therewith. Typically, the tie layer may comprise a graft polymer of maleic anhydride with propylene, especially isotactic polypropylene. Desirably, the external layer of plastics material (iii) directly adhered to layer ii) may comprise isotactic polypropylene. Furthermore, the internal layer of plastics material iv) may comprise isotactic polypropylene. Suitably, layer v) may comprise isotactic polypropylene.

The oxygen scavenger may be any of the proprietary products available as such and which often incorporate polyhydroxy phenolic derivatives. Alternatively, they may include a transition metal in a lower oxidation state, for example Fe(II) which is oxidised to a higher oxidation state by trace oxygen which is thereby scavenged. The transition metal may be suitably masterbatched; for example with the plastics material, such as polypropylene, used. SHELFPLUS, especially SHELFPLUS 2500 has been found to be very suitable.

The sheet according to this invention may be preparable by coextrusion. Desirably, it may have a thickness from 400 to 2500, such as 1000 to 1500, μm as prepared and from 200 to 400 μm after fabrication into a container.

In accordance with a preferred feature of this invention layer i) may comprise from 2.5 to 10%, preferably 3.0 to 8%, such as 6.5%, of the thickness of the sheet. Each tie layer ii), which may be the same or different, may comprise from 1 to 3%, such as 2% of the thickness of the sheet. The, or all of the, layer(s) iii) may comprise from 30 to 20% of the thickness of the sheet. Preferably, layer iii) does not include any added oxygen scavenger. The layer iv) may comprise from 35 to 55 %, such as 43 %, of the thickness of the sheet. Preferably, layer iv) comprises from 2 to 8%, such as 5%, by weight of oxygen scavenger. Below 2% the scavenger is unlikely to be effective while above 8% the scavenger has no additional effect and may adversely effect the mechanical properties of the sheet. The scavenger is suitably first masterbatched with the plastics material from which (iv) is fabricated. Layer iv) may comprise up to 100% by weight of regrind, typically 50% by weight of regrind. Preferably, layer v) comprises from 15 to 25%, such as 16.5% of the thickness of the sheet.

In accordance with an especially preferred embodiment of this invention, it is found that particularly beneficial effects are obtained when the gas barrier layer i) comprises from 3.0 to 8% of the thickness of the sheet while the concentration of oxygen scavenger in layer iv) comprises from 3 to 7% by weight of layer iv).

In accordance with a further aspect of the invention, there is provided a sheet according to the invention formed as a container. Preferably, the container is thermoformed.

It is highly desirable that the container of the invention may be subject to microwave radiation without loss of dimensional stability. Thus, the components of the layers, as fabricated, must not melt when irradiated with microwaves.

This invention also provides such containers which are filled and hermetically sealed. The sealing is preferably effected with a closure, such as a lid, fabricated from a sheet according to the invention. Suitably, the fill comprises a comestible or a beverage product. Desirably, the

filled, sealed container is then sterilised, for example by autoclaving.

The invention is further illustrated, by way of example, with reference to the sole Figure which is a diagrammatic cross-section of the sheet according to this invention.

The production line includes blending equipment (eg. COLORTRONIC OR MAGUIRE blenders) for separately blending five different feedstocks. These feedstocks are then fed to five different extruders (eg. EGAN or KUHNE extruders) in which the material is heated, pressurised and mixed and next the five streams are fed, without mixing, to a layer delivery block which assembles the layers. A typical melt temperature is about 200°C. The molten multilayer structure is then spread through a die assembly which delivers a molten multilayer sheet to a cooled calender roll stack where the sheet is next solidified prior to being wound on to reels.

The sheet comprises an external layer (1) comprising 30 % of the total thickness and comprising isotactic polypropylene and a copolymer of propylene (such as MONTEL T31SE and MONTEL EPT30R, respectively); a tie layer (2) comprising 2 % of the total thickness and comprising a maleic anhydride-polypropylene graft copolymer (such as ADMER QF55IE); a barrier layer (3) comprising 6.5 % of the total thickness and comprising ethylene-vinyl alcohol of 32 % by weight polymerised ethylene content (such as EVAL T101B); a tie layer (4) as in (2); an internal layer (5) comprising 43 % of the total thickness and comprising regrind including a total of 5 % oxygen scavenger (such as SHELFPLUS 2500); a further layer (6) as in (1), but comprising 16.5 % of the total thickness.

Containers are formed from the sheet using a thermo forming process in which a combination of air pressure, temperature and a mechanical forming assist or plug are used to fabricate the sheet in a thermoformer (eg ILLIG 70k) into the desired form for the container. Typical forming temperatures are around 180°C to 185°C such as 183°C.

The shelf life of the food with which the containers are filled and hermetically sealed can be in excess of 18 months. Significantly inferior results were obtained when the scavenger was included in layer iii) but not in layer iv).

CLAIMS

1. A multi-layer plastics sheet which comprises
 - i) a gas barrier layer;
 - ii) a tie layer disposed contiguously on either side of layer i);
 - iii) one or more external layers of plastics material adhered contiguously to one of the tie layers ii); and
 - iv) an internal layer of plastics material which includes an oxygen scavenger, the layer being adhered contiguously to the other of the tie layers ii).
2. A sheet according to claim 1 which further comprises a layer of plastics material v) contiguously adhered to layer iv) and not including an oxygen scavenger.
3. A sheet according to claim 1 or 2 wherein layer i) comprises polyvinyl alcohol or an ethylene-vinyl alcohol copolymer.
4. A sheet according to claim 3 wherein the degree of hydrolysis of the polyvinyl alcohol is from 70 to 90%.
5. A sheet according to claim 3 wherein the vinyl alcohol content of the ethylene-vinyl alcohol copolymer is from 50 to 75%.
6. A sheet according to any preceding claim wherein each tie layer ii) comprises a graft copolymer of an unsaturated carboxylic acid or unsaturated carboxylic acid anhydride with the polymer of the plastics material contiguous therewith.
7. A sheet according to any preceding claim wherein the external layer of plastics material (iii) directly adhered to layer ii) comprises isotactic polypropylene.

8. A sheet according to any preceding claim wherein the internal layer of plastics material iv) comprises isotactic polypropylene.
9. A sheet according to any one of claims 6 to 8 wherein layer ii) comprises a graft copolymer of maleic anhydride with polypropylene.
10. A sheet according to any one of claims 2 to 9 wherein layer v) comprises isotactic polypropylene.
11. A sheet according to any preceding claim wherein the oxygen scavenger comprises a polyhydroxy phenolic compound.
12. A sheet according to any preceding claim preparable by coextrusion.
13. A sheet according to any preceding claim which has a thickness from 400 to 2500 μm .
14. A sheet according to any preceding claim wherein layer i) comprises from 2.5 to 10% of the thickness of the sheet.
15. A sheet according to any preceding claim wherein each tie layer ii), which may be the same or different, comprises from 1 to 3% of the thickness of the sheet.
16. A sheet according to any preceding claim wherein the, or all of the layer(s) iii) comprise(s) from 30 to 20% of the thickness of the sheet.
17. A sheet according to any preceding claim where the layer iv) comprises from 35 to 55% of the thickness of the sheet.

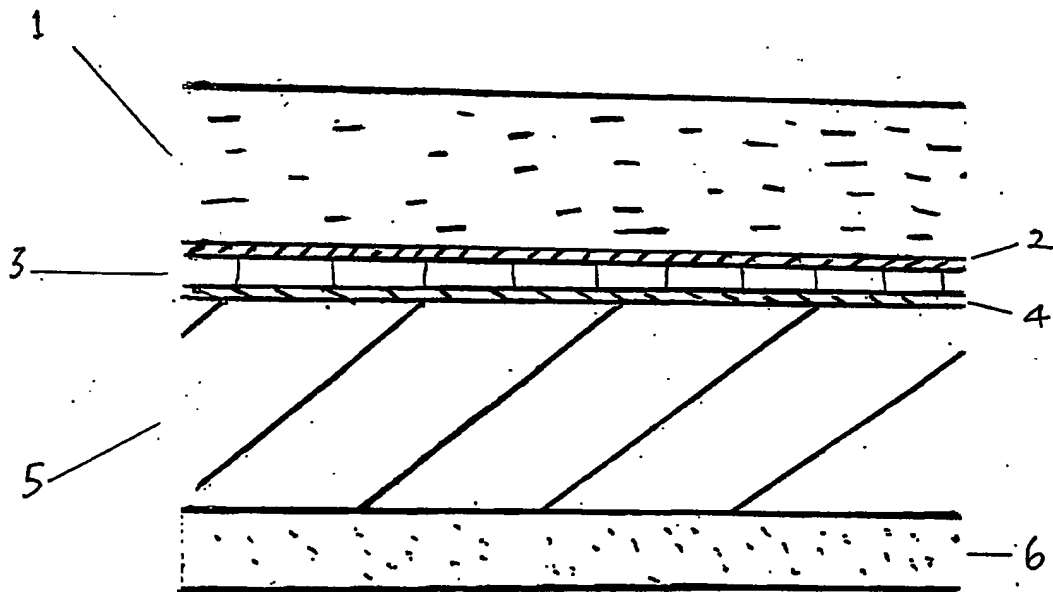
18. A sheet according to any preceding claim wherein the layer iv) comprises from 2 to 8 % by weight of oxygen scavenger.
19. A sheet according to any preceding claim wherein the layer iv) comprises from 20 to 80 % by weight of regrind.
20. A sheet according to any one of claims 2 to 19 wherein layer v) comprises from 15 to 25 % of the thickness of the sheet.
21. A sheet according to any preceding claim formed as a container.
22. A sheet according to claim 21 wherein the container is thermoformed.
23. A container according to claim 21 or 22 which may be subject to microwave radiation without loss of dimensional stability.
24. A container according to claim 23 which is filled and hermetically sealed.
25. A container according to claim 24 wherein the sealing is effected with a closure fabricated from a sheet according to any of claims 1 to 20.
26. A container according to claim 24 or 25 wherein the fill comprises a comestible or a beverage product.
27. A filled sealed container according to any of claims 24 to 26 which is then sterilised.
28. A filled sealed container according to claim 27 wherein the sterilisation is effected prior to sealing with hydrogen peroxide or is effected after sealing with steam or with pressurised

water at a temperature above 100°C.

29. A sheet according to claim 1 substantially as herein before described with reference to the Figure.

30. A container according to claim 23 substantially as hereinbefore described.

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Fig. 1

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PCT/GB 01/03750

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B32B27/08 B65D81/26 A23L3/3436

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B32B A23L B65D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 536 409 A (FARRELL CHRISTOPHER J ET AL) 20 August 1985 (1985-08-20) column 6, line 55 - column 7, line 9 column 1, line 5 - line 7 column 3, line 65 - column 4, line 6 column 6, line 13 - line 15 ---	1-30
X	US 5 274 024 A (KOYAMA MASAYASU ET AL) 28 December 1993 (1993-12-28) column 7, line 1 - line 12; figure 3 --- -/--	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

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O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

G document member of the same patent family

Date of the actual completion of the international search

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

De Jonge, S

INTERNATIONAL SEARCH REPORT

International Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p> DATABASE WPI Section Ch, Week 199310 Derwent Publications Ltd., London, GB; Class A92, AN 1993-079979 XP002182127 & JP 05 024146 A (TOPPAN PRINTING CO LTD), 2 February 1993 (1993-02-02) abstract </p>	6,9

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PC/GB 01/03750

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4536409	A	20-08-1985	AU 554572 B2	28-08-1986
			AU 7837481 A	29-07-1982
			BR 8200330 A	23-11-1982
			CA 1164847 A1	03-04-1984
			ES 508996 D0	01-04-1983
			ES 8304485 A1	01-06-1983
			GR 76515 A1	10-08-1984
			IL 64280 A	31-08-1986
			IN 157118 A1	18-01-1986
			JP 4062858 B	07-10-1992
			JP 57146651 A	10-09-1982
			KR 8901417 B1	03-05-1989
			MX 170718 B	09-09-1993
			MX 157008 A	19-10-1988
			NZ 199106 A	13-09-1985
			PH 20637 A	16-03-1987
			US 4702966 A	27-10-1987
			ZA 8107950 A	23-02-1983
US 5274024	A	28-12-1993	JP 2308852 A	21-12-1990
			JP 7033475 B	12-04-1995
			AU 634236 B2	18-02-1993
			AU 5544990 A	18-12-1990
			EP 0428736 A1	29-05-1991
			WO 9014392 A1	29-11-1990
JP 5024146	A	02-02-1993	JP 2844977 B2	13-01-1999